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Dielectric behavior during sol-gel transition of PEO-PPO-PEO triblock copolymer aqueous solution

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Thermoreversible sol-gel transition of the PEO-PPO-PEO triblock copolymer(Pluronic F127) aqueous solution was monitored by dielectric behavior measurement. Thermoreversible gelation originates from the micelle formation and micelle volume change due to PEO-water, PPO-water LCST behavior. Micelle volume fraction is the critical parameter that dominates the sol-gel transition behavior of Pluronic aqueous solution. By measuring the dielectric constant of 5-22% Pluronic F127 aqueous solution, critical micelle temperature and micelle volume fraction was obtained. The micelle volume fraction of the gel region exceeded the critical volume fractions of simple cubic packing (0.523). Gelation temperature determined by dielectric measurement agreed well with that determined by the tube tilting method.

Introduction

Temperature-sensitive sol-gel transition and micellization of PEO-PPO-PEO triblock copolymer (Pluronic®, BASF) aqueous solution has been studied by many authors since Schmolka(1) reported its interesting thermoreversible sol-gel transition. At low temperature, Pluronic F127 is homogeneous unimer solution as PPO-water interaction is favorable. As temperature increases, PPO-water interaction becomes unfavorable, PPO collapses into the micelle core. As temperature increases, number of micelles increases. Above the critical micelle concentration and temperature, sol-gel transition occurs(low T_{gel}). High modulus of the gel is ascribed to the repulsive micelle-micelle interaction(2) above gelation concentration and temperature. At higher temperature, interaction of PEO and water becomes unfavorable, therefore, gel-to-sol transition(high T_{gel}) occurs due to dehydration and shrinking of PEO shell. Above PEO-water LCST temperature, phase separation between polymer and water is observed.

In the micelle system of Pluronic aqueous solution, micelle volume fraction is the critical parameter that determines the sol-gel transition temperature. There have been many studies that deals with micelle volume fraction using the light scattering, small angle neutron scattering(3-4,9) considering hard sphere interaction model. Rheological study on the sol-gel transition has also been reported(4).

However, there has been no attempt to obtain micelle volume fraction of Pluronic solution using dielectric measurement. Micelle system of Pluronic F127 hydrogel can be considered as a heterogeneous polymer system where copolymer micelles are dispersed in the medium. Volume fraction and dimension of dispersed phase can be obtained by

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dielectric measurement(5).

In the present study, we measured the change of dielectric constant during the micellization and sol-gel transition of Pluronic F127 aqueous solution and intended to calculate the micelle volume fraction using Hanai's relationship(6). Calculated micelle volume fraction was compared to those obtained by SANS etc.(9)

Experimental

Pluronic F127(BASF) was dissolved in methylene chloride, precipitated in diethyl ether and dried under vacuum for 2 days before experiment. Pluronic F127 aqueous solution was prepared by dissolving the Pluronic in the Milli-Q water (conductivity = $1.6\text{x}10^{-6}$ S/cm). The concentration of Pluronic F127 solution prepared was 5, 10, 14, 16, 18, 20 and 22 % by weight.

Using impedance analyzer (Impedance Analyser 1260, Solartron) and homemade liquid dielectric cell (Figure 1), complex impedance was measured from 0.1MHz to 10MHz. Impedance measurement was carried out from 5°C to 92°C at the heating rate of 0.8°C/min using temperature controllable water circulating chamber. To prevent water evaporation from the solution, the cell was sealed with vacuum grease. Dielectric cell was calibrated with reference liquids according to standard procedure(8).

Dielectric constant was calculated with the following equation

$$e^* = \frac{1}{j\omega C_0 Z^*} \qquad (1)$$

where C_0 is the capacitance of the empty cell,
Z^* is the complex impedance,
e^* is the complex dielectric constant,
ω is the angular frequency(=2πf),
j is square root of -1.

Hanai equation (eq. (2)) provides the relationship between the volume fraction of the suspended spheroid particles and the dielectric constant of the solution, micelles and medium (6-7).

$$\frac{e' - e_2'}{e_1' - e_2'}\left(\frac{e_1'}{e'}\right)^{1/3} = 1 - v_2 \qquad (2)$$

where e' is the dielectric constant of the solution,
e_1' is the dielectric constant of the medium,
e_2' is the dielectric constant of the dispersed spheroid,
v_2 is the volume fraction of the dispersed spheroid.

Sol-gel transition temperature of the sample was measured by the conventional tube tilting method.(10)

Results and Discussion

Generally, the aqueous solution of polymer such as protein aqueous solution shows three dielectric relaxations(11). It is known that around 10GHz the dielectric relaxation of the free water molecules (γ transition) occurs, around 100MHz, dielectric relaxation of the bound water (δ transition) occurs, and around 1MHz, dielectric relaxation of the

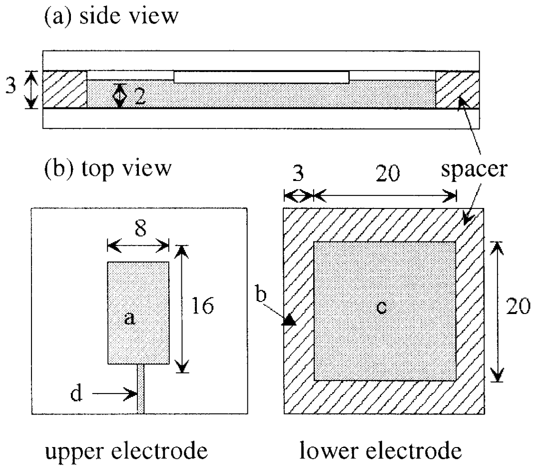

Figure 1. Schematic diagram of liquid dielectric cell (a) side view (b) top view ; a, gold coated glass electrode, b, PEI spacer, c, gold coated ceramic electrode, d, gold electric line (unit:mm)

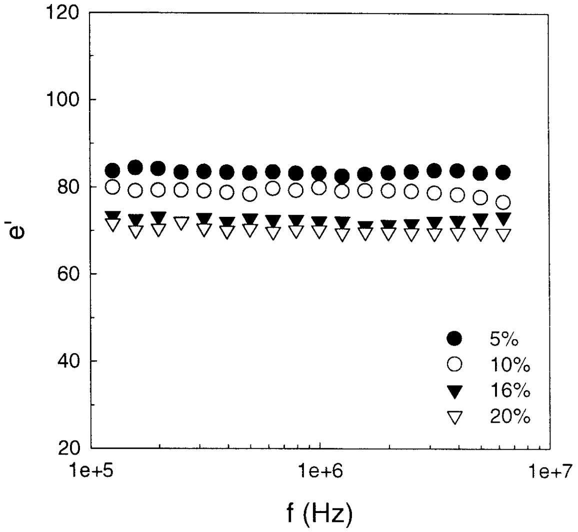

Figure 2. Dielectric constant of Pluronic F127 solution as a function of frequency at 5°C

macromolecular species(β transition) occurs.

The value of dielectric constant was nearly constant in the experimental frequency range(Figure 2). For convenience, dielectric constant at 1.2MHz was used in the further calculation as the solution dielectric constant.

For a solution with spherical particles, Hanai derived an equation relating the dielectric constant of the solution (eq.2), dispersed micelle and the volume fraction of the micelle. Hanai's equation has been verified for several systems such as water in oil (6), mitochondria in the buffer solution(7) etc.

Figure 3 shows the dielectric constant of Pluronic F127 aqueous solution measured at 1.2MHz.

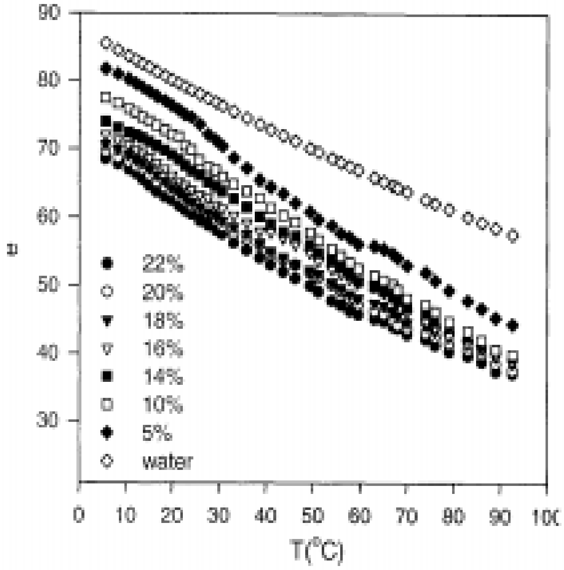

Figure 3. Dielectric constant of Pluronic F127 aqueous solution at 1.2MHz

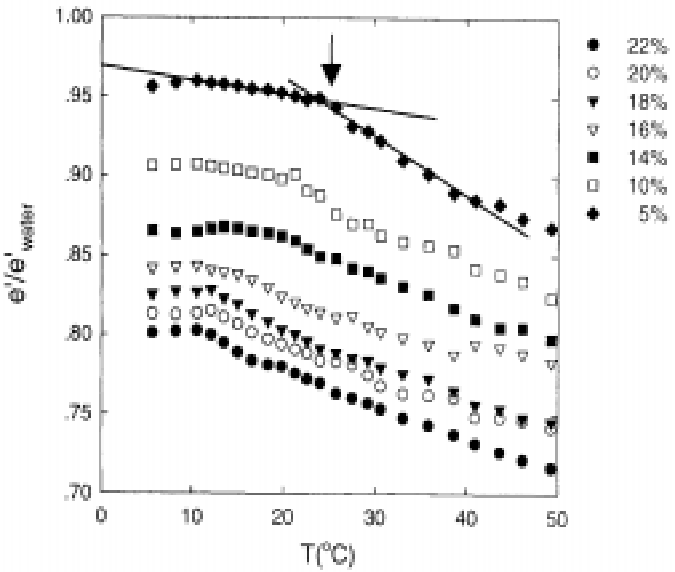

Figure 4. Dielectric constant of Pluronic F127 solution normalized by water dielectric constant

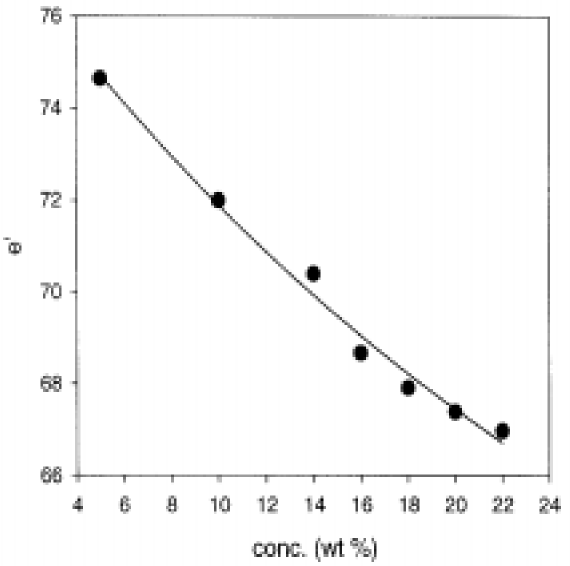

Figure 5. Dielectric constant of Pluronic F127 solution at critical micelle temperature

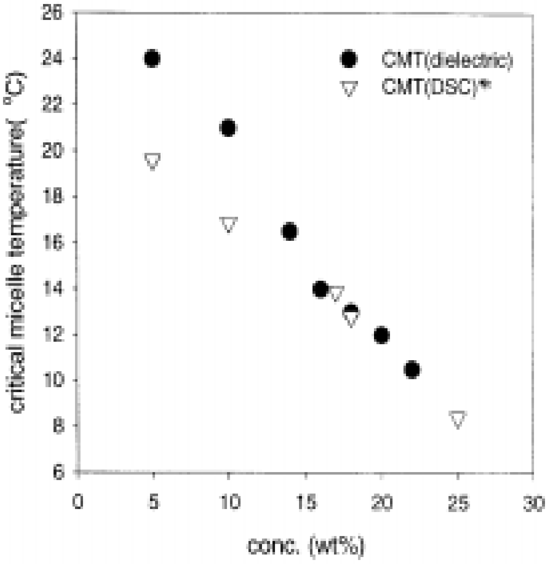

Figure 6. Critical micelle temperature of Pluronic F127 solution determined by dielectric measurement and DSC (*,Wanka et al.(3))

Critical micelle temperature(CMT)

Figure 4 shows the dielectric constant normalized by the water dielectric constant. CMT was observed from the change of the slope of the normalized dielectric constant.

Solution dielectric constant at CMT is a function of concentration and CMT itself that is also a function of concentration. Figure 5 shows the solution dielectric constant at CMT as a function of concentration. The concentration dependency of dielectric constant at CMT can be expressed as equation (3).

$$e'_{CMT} = 55.964 + 22.101\exp(-0.033c) \qquad (3)$$

where c is the concentration of Pluronic F127 solution(wt%).

The CMT obtained from the dielectric measurement is compared with CMT obtained from DSC by Wanka et al(3). Both data agreed quite well. Particularly at high polymer concentration (over 14%), there was excellent agreement between dielectric analysis and DSC analysis(Figure 6).

From the critical micelle temperature, PPO phase separation starts due to decreasing PPO-water interaction, which induces micelle formation with PPO core and PEO shell. Increasing hydrophobic interaction of PPO might reduce the dielectric constant of the solution.

Medium dielectric constant

From CMT, unimer to micelle transition starts. With increasing temperature, equilibrium shifts from the unimer dominant solution to the micelle dominant solution. From CMT to maximum packing temperature(MPT), triblock copolymer exists in the medium as unimer and micelle solution. MPT is considered as the temperature where all unimers are incorporated into micelles. Above MPT, there is no unimer in the medium, therefore, medium dielectric constant is that of pure water.

Medium dielectric constant from CMT to MPT was assumed to change linearly. It was also assumed that the MPT was 50°C which was the mid point temperature of two sol-gel transition temperature in the symmetric phase diagram. Figure 7 shows the medium dielectric constant and micelle dielectric constant. Dotted line denotes the calculated medium dielectric constant of Pluronic solution between CMT and MPT.

Micelle dielectric constant

Micelle dielectric constant is unknown in equation(2). For 20% sample, we could calculate two e_2' values at two gel temperatures at which micelle volume fraction was considered as that of the simple cubic packing of spherical particles(0.523). Micelle dielectric constant was assumed to the linear function determined by two $e_2'(T_{gel})$s. Referring to SANS study of Mortensen et al.(9), micelle volume fraction was higher than 0.523 between two sol-gel transition temperatures.

Solid line in Figure 7 is the calculated micelle dielectric constant from 20% data assuming micelle volume fraction is equal to that of the simple cubic packing of spherical particles(0.523) at two gelation temperatures. For other concentration, the micelle dielectric constants calculated at its own T_{gel} lie on the solid line quite well.

This implies that the micelle dielectric constant depends only on the temperature, not on the concentration.

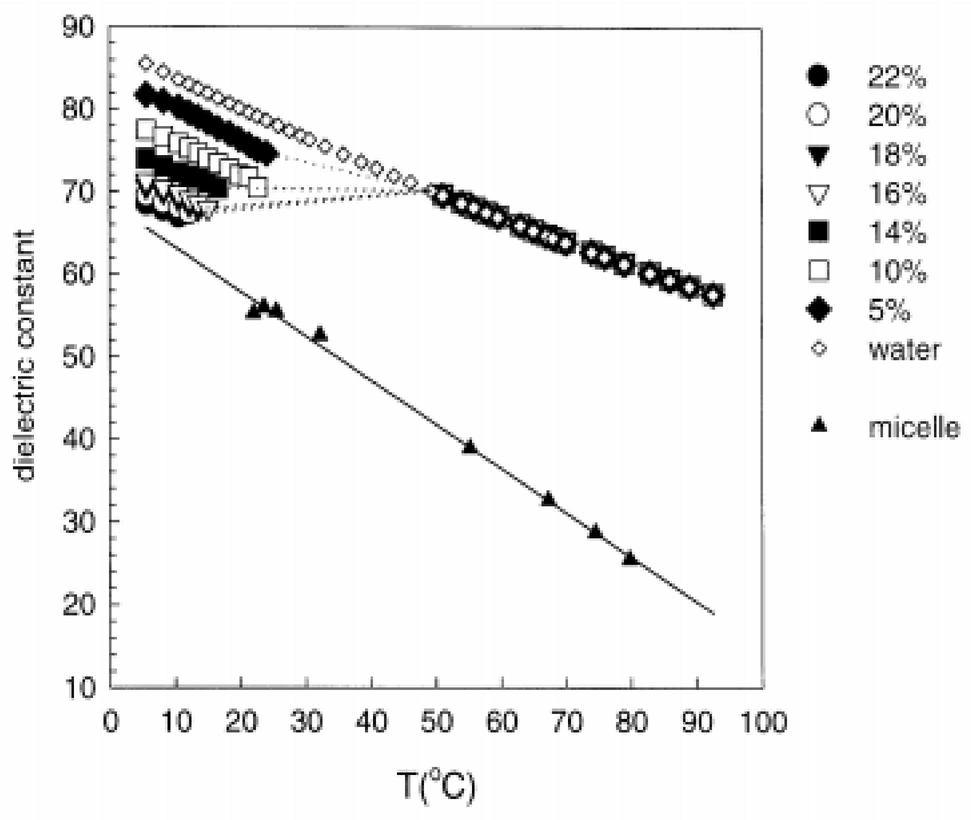

Figure 7. Dielectric constant of medium and micelle

Micelle volume fraction

Thermoreversible sol-gel transition of Pluronic F127 aqueous solution originates from micelle formation and micelle volume change owing to PEO/water, PPO/water LCST behavior (2). Above LCST temperature of PPO, micelle with PPO core and PEO shell appears. As temperature increases, number of micelles increases. Above critical micelle volume fraction (0.523), we can observe gel phase. Gel phase is ascribed to the repulsive micelle-micelle interaction(3) above critical micelle volume fraction. At high temperature, interaction of PEO and water is unfavorable, therefore, gel-to-sol transition occurs due to dehydration and shrinking of PEO shell. Above PEO-water LCST temperature, phase separation between polymer and water is observed.

Figure 8 shows the micelle volume fraction calculated by Hanai equation with solution dielectric constant, medium dielectric constant and micelle dielectric constant. It shows that in the gel region micelle volume fraction is higher than the critical volume fraction (0.523). Referring to Mortensen and Talmon's SANS study(9), in the gel state region, micelle volume fraction exceeded the critical value, 0.523. SANS measurements also showed that the gel regime was an ordered structure due to close packing of micelles in cubic structure (9,12). At even higher temperatures a hexagonal phase was observed(12) due to change of polymer-water interaction.

When the concentration of Pluronic micelle is high enough to exceed the volume fraction of hexagonal close packing(0.74), rod-like micelle or lamellae morphology etc. probably appears.

In the present study, micelle dielectric constant of 20% was calculated on the basic assumption that at gel temperature micelle volume fraction is higher than 0.523. For other concentration samples, micelle volume fraction was higher than 0.523 in the gel region and showed good fitting with sol-gel transition temperature obtained from the tube tilting method(Figure 9), which means that the micelle dielectric constant is independent of concentration and the dimension of the micelle and the composition of polymer and water in the micelle are not a function of concentration but temperature.

Figure 9 shows the sol-gel transition phase diagram which contains observed T_{gel} measured by conventional tube-tilting method and calculated T_{gel} by dielectric measurement. T_{gel} calculated by dielectric measurement agrees well with that obtained by tube-tilting method.

Conclusion

Measuring dielectric constant of Pluronic F127 aqueous solution, critical micelle temperature was determined, which was ascribed to decreasing hydrophilicity of the PPO block in the aqueous medium at critical micelle temperature. By measuring the dielectric constant of Pluronic F127 aqueous solution, micelle volume fraction was also calculated. T_{gel} was obtained from the temperature at which micelle volume fraction exceeded the critical value(0.523). Gelation temperature determined by dielectric measurement agreed well with that determined by the tube tilting method. For experimental concentration range, micelle dielectric constant was independent of concentration and only changed with temperature, which implied that the micelle dimension and composition depended on the temperature, not on the concentration.

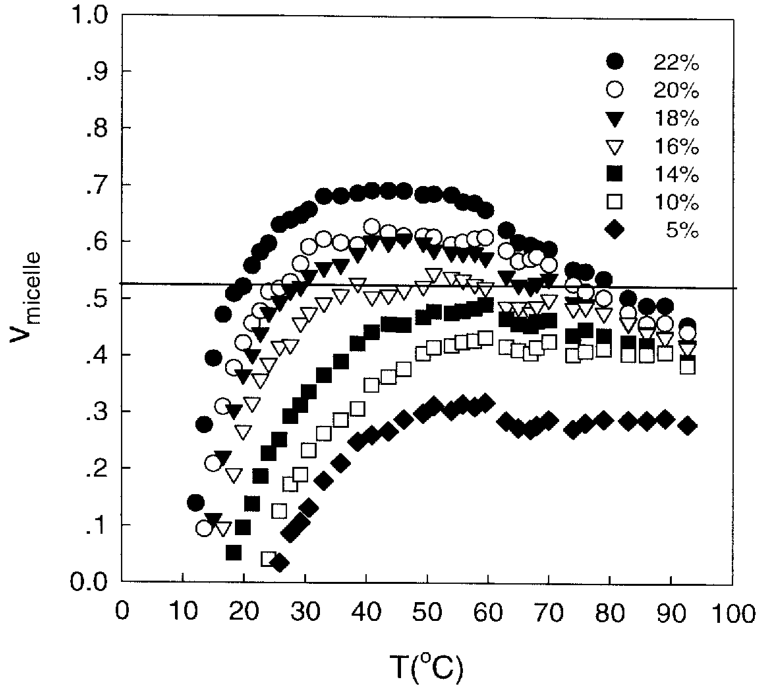

Figure 8. Micelle volume fraction of Pluronic F127 solution with varying concentration

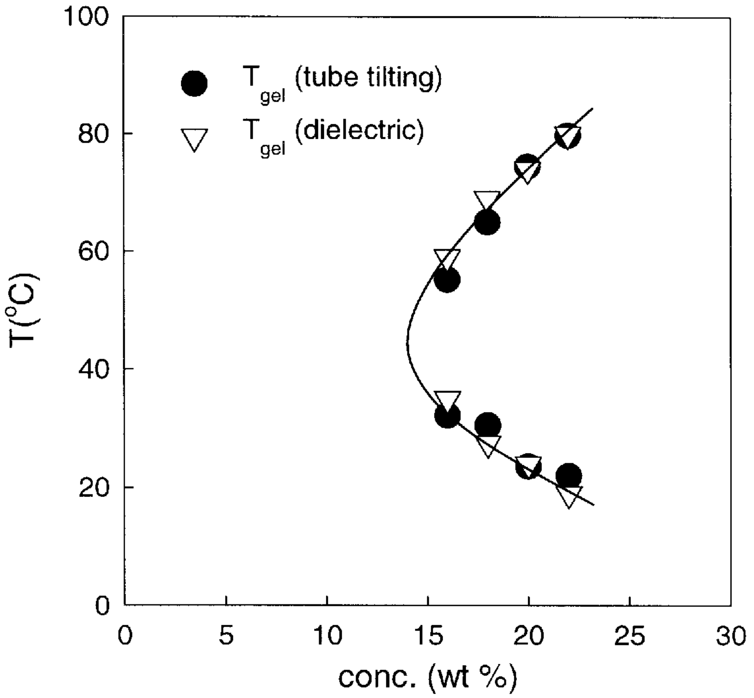

Figure 9. Sol-gel phase diagram of Pluronic F127 aqueous solution determined by tube tilting method and dielectric measurement

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